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Luminescence of ultrafine magnesium oxide ceramics with deep traps

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Abstract. Thermoluminescence (TL) of ultrafine anion-defective magnesium oxide ceramics with a grain size of about 150 nm, which were thermally treated in highly reducing conditions at T=1100–1400 ^{o}C, has been studied after high-dose irradiation with a pulse electron beam (130 keV). Thermal treatment was found to cause TL intensity grow, which is associated with an increasing concentration of F-type centers. It was shown that varying occupancy of deep trapping centers changes a yield of the TL peak at 380 K. A hypothesis was made that the traps which are responsible for the TL peak at 380 K mainly have a hole nature in the samples under study.

1. Introduction

Luminescence properties of phosphors are predominantly determined by the processes of charge transfer between different localized states including the ones associated with deep trapping centers [1]. The competing processes in charge trapping by deep traps cause a number of effects essential for applications of many technically important phosphors in particular metal oxides (α-Al_2O_3, SiO_2, BeO). These effects include changes in the luminescence yield (sensitization and desensitization) after radiation treatment [2-5], and non-linear dependences of thermoluminescence (TL) intensity on the absorbed dose of ionizing radiation [3,6]. Moreover, a temperature dependence of competing effect of deep centers can cause luminescence quenching and a resulting drop in the TL yield with an increasing heating rate of the material [7], which should not be neglected in TL dosimetry.

Deep trapping centers are present in such phosphor as magnesium oxide (MgO). An interest in the study of its luminescent properties is due to a possibility of its use as a TL detector of gamma-, UV- and neutron radiations [8-10]. Deep traps in the material are detected through TL measurements in the range of 450–800 K [10,11], and also indirectly via measurements of phototransferred TL [12]. From the data obtained with the use of EPR method, it was found that a number of high-temperature TL peaks are associated with destruction of hole V-type centers connected with cation vacancies and more complex H-centers [10,11]. However, many aspects of the charge transfer processes with deep traps involved, which cause changes in TL sensitivity to ionizing radiation, are little studied and require further research. Improving TL sensitivity is especially important for ultrafine modification of magnesium oxide, as phosphors with small sizes of grains are usually less TL sensitive to radiation in comparison with their bulky analogs [13,14]. Furthermore, the study of TL properties of ultrafine MgO is of special interest because nanophosphors are promising materials for high-dose (over 1 kGy) dosimetry due to their high radiation resistance [13,14].

The aim of this work is to study luminescent properties of ultrafine magnesium oxide, which are associated with deep traps.

2. Samples and Experimental Methods

The studied MgO samples were in the form of compacts 5 mm in diameter and 1 mm thick made of nanopowder using the method of uniaxial cold pressing at a unit pressure of 1000 kgf/cm^2. The precursor powder with the grain size of 45–75 nm was produced by "Plasmoterm" (Moscow, Russia) by plasma synthesis method. The proportion of MgO was 99.8 weight%. The powder contained Fe_2O_3 (not more than 0.1%) and SiO_2 (not exceeding 0.1 %) impurities.

To increase the luminescence yield, the precursor compacts were exposed to high temperatures (T=1100–1400 ^{o}C for three hours) in vacuum (10^{-3}–10^{-4} Torr) in reducing conditions. The conditions are created due to the presence of carbon as a graphite rod. The reported thermal treatment of the materials based on wide-gap oxides causes increased concentrations of F-type centers in these materials, where these centers are associated with oxygen vacancies which determine luminescent properties of this class of materials [15,16]. It is known that when nanosized materials are treated with high temperatures, nanoparticles stick together to form larger particles [17]. An X-ray diffraction method was used to measure the sizes of nanoparticles in thermally treated MgO compacts. X-ray diffraction studies of nanopowder compacts were carried out with Shimadzu XRD Maxima-7000 diffractometer. Imaging was performed in Cu-K$\alpha_{1,2}$-radiation in scan-step mode with $\Delta(2\theta) = 0.03°$ in the 2θ angle range from 15 to 115°, exposition time in each point was 3 s.

To excite TL, the samples were exposed to a pulsed electron beam from an accelerator (pulse time 2 ns, mean electron energy (130±1) keV, current density 60 A/cm^2) at room temperature. An absorbed dose from one pulse was found experimentally with a film dosimeter PD(F)R-5/50 and was 1.5 kGy/pulse [18]. A source of beta-radiation BIS-10 on the base of ^{90}Sr/^{90}Y isotopes with the dose rate of 8 mGy/min was also used in the experiments. TL was measured at linear heating with the rate of 2 K/s by using FEU-130 photomultiplier tube with the maximum spectral sensitivity of 400–420 nm. An experimental facility for measuring TL spectra is described in [19].

3. Results and Discussion

Figure 1 presents X-ray diffraction pattern of magnesium oxide compacts which were annealed at the maximum temperature T=1400 ^{o}C. The obtained results show that the samples under study contained a cubic phase (space group $Fm\bar{3}m$). Miller indexes related to different diffraction peaks are also given in figure 1.

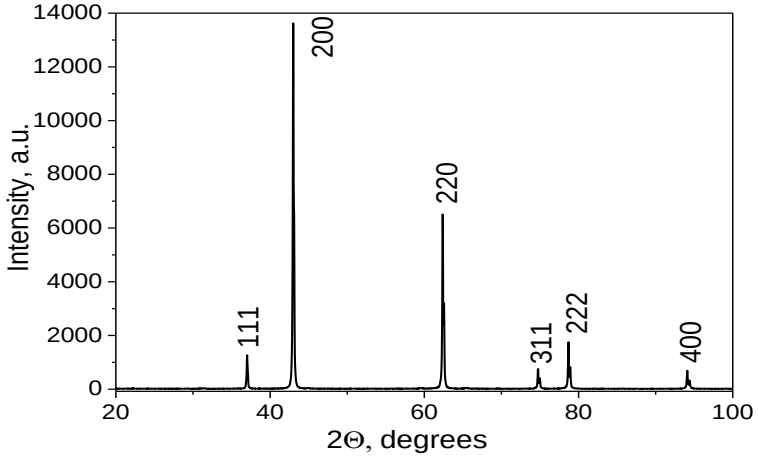

Figure 1. X-ray diffraction pattern of the magnesium oxide compacts thermally treated at 1400 ^{o}C

The particle sizes in the samples under study were determined following broadening of the diffraction peaks by using Williamson-Hall method [20]. The observed peak broadening in nanomaterials can be caused by inhomogeneity, breaking of translation symmetry of the crystalline structure and of some elements of point symmetry due to small sizes of the particles. To approximate the profile of the diffraction peaks, the pseudo-Voigt function, which is a weighted superposition of Gaussian and Lorentz functions, was chosen. The peak broadening was determined taking into account the resolution of the device.

Figure 2 shows dependence of the given broadening of peaks on the magnitude of scattering vector for magnesium oxide compacts, which were thermally treated at the maximum temperature (1400°C). It can be seen that broadening grows when the scattering vector becomes longer. This means that broadening is affected not only by particle sizes, but also by micro-deformations of the crystalline lattice. Then, the value of the given broadening β_0 in the crossing point of the straight line with the axis of ordinates was found by extrapolating linear dependence which approximates the experimental points. The particle size was calculated as a reciprocal value of β_0 and was about 150 nm. The results obtained show that thermally treated MgO compacts are ultrafine ceramics.

Figure 3 presents TL curves on a logarithmic scale of the studied MgO compacts (both initial and synthesized at different temperatures) after exposure to a pulsed electron beam (30 kGy). The TL curve of the initial samples features three peaks. Peak A has the maximum at 380 K; it is considered as the main one further on. Peak *B* at 510 K and peak *C* at 630 K, which are associated with deep traps are also seen on the TL curve. The data in figure 3 show that high-temperature annealing in the reducing environment leads to greatly increased TL yield in peak *A* (by more than two orders of magnitude). One can hypothesize that TL intensity grows due to increased concentration of anion defects which create luminescence F-type centers in different charge states. Formation of F- and F^+-centers in the thermally treated compacts under study in our work was verified before by using luminescence spectroscopy [21].

A growing TL yield is also observed in the temperature range of deep traps luminescence (450–670 K) after high-temperature annealing. Emergence of the regions where TL intensity only slightly depends on temperature on the TL curves is an interesting characteristic of TL of the thermally treated samples. To clarify the TL mechanism responsible for such curves, we preliminary measured isothermal decay of the TL samples which were thermally treated at different temperatures [21]. We found that decay kinetics did not depend on the temperature of isothermal exposure, and the TL decay curves were described with hyperbolic function of $I(t)=K/t$-type.

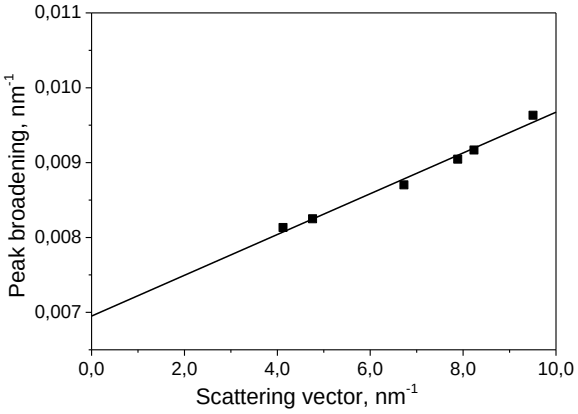

Figure 2. Dependence of the given broadening on the magnitude of the scattering vector for magnesium oxide compacts thermally treated at 1400 °C

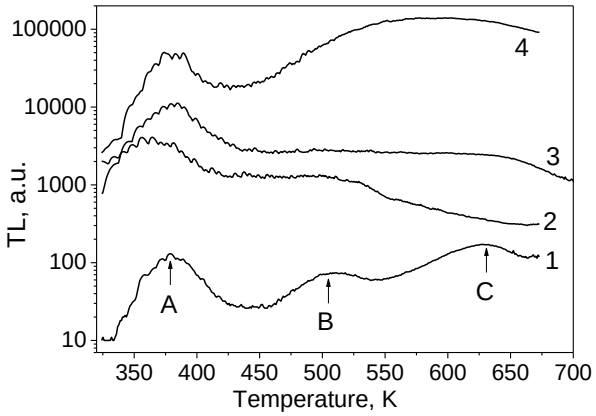

Figure 3. TL of magnesium oxide after exposure to a dose of 30 kGy with a pulsed electron beam: precursor compacts (1); thermally treated compacts at 1200 °C (2); at 1300 °C (3); at 1400 °C (4)

The results obtained confirm the fact of existence of the tunneling mechanism of recombination of charge carriers which were released from the deep traps. The reported mechanism was earlier studied in YPO_4 doped with different impurities [22]. For more details of this effect in magnesium oxide further studies are required.

In addition, we studied an effect of deep traps occupancy on the intensity of the main TL peak at 380 K. MgO ceramics samples thermally treated at 1200°C were used. Deep traps were preliminary filled with 50 pulses of an electron beam (75 kGy) at room temperature. After exposure to an electron beam, the samples were annealed up to 470 K till the traps responsible for the main peak at 380 K were completely emptied. The measurement cycle was as reported below. In the samples with filled deep traps, TL of the main peak was excited with a low dose of beta-radiation (40 mGy) and was recorded at 325–475 K. After that, the samples were annealed up to T_{ann} to partly empty the deep traps. T_{ann} temperature increased with a constant step (20 K) and changed within the range of 470–730 K in every cycle.

Figure 4 shows a dependence of the intensity of the TL peak at 380 K on the temperature of the stepped annealing (curve 1). 1.0 a.u. level is related to the initial TL sensitivity before filling of the deep traps. Curve 2 is TL of the deep traps, which was obtained after thermal cleaning up to T=470 K at a heating rate of 2 K/s to exclude the effect of the TL peak at 380 K. It can be seen that when the deep traps are filled, the intensity of the TL peak at 380 K increases by approximately one order of magnitude. When the deep centers responsible for TL peaks at 510 and 600 K are emptied further, desensitization of TL at 380 K is observed. At T_{ann}=730 K, TL sensitivity returns to its initial value before high-dose irradiation.

This effect can be explained through the model of competing traps capturing carriers of the same sign [23]. Filling of the deep traps decreases the probability of competing trapping of the charge carriers by these traps and leads to a growing number of events of emission recombination on the luminescence centers, which causes sensitization of TL of the main traps responsible for the TL peak at 380 K. Decreasing occupation of the deep centers under stepped annealing, on the contrary, conditions decreasing possibility of radiative transitions and, therefore, desensitization of TL. Such mechanism of changing TL sensitivity, which is associated with a competing effect of deep centers at the stages of irradiation and thermal stimulation, has been observed before in other wide-gap oxide phosphors (Al_2O_3, SiO_2) [2,3,5]. In ultrafine magnesium oxide the effects of TL sensitization/desensitization have been found by us for the first time.

Learning more about the details of the charge transfer processes, the sign of the charges and the nature of the defects associated with the traps of the main TL peak and deep traps in the compacts under discussion in this paper requires further study. What we can state so far is the following.

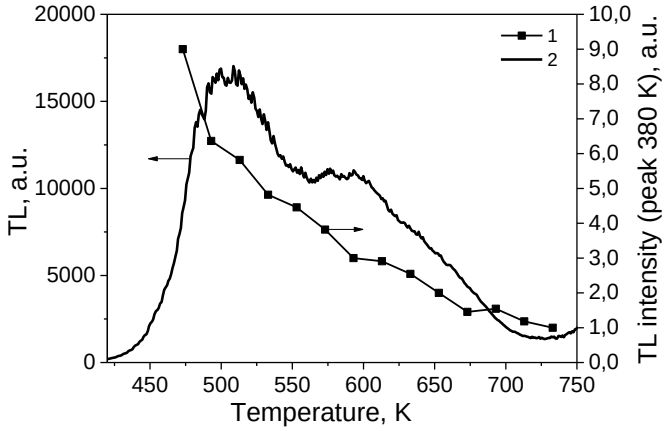

Figure 4. Dependence of the intensity of the TL peak at 380 K on the temperature of the stepped annealing (T_{ann}) which gradually makes deep traps empty (1); TL curve of deep centers (2)

There are data from the literature, which are based on the measurements of EPR spectra, that the TL peak at 380 K is caused by releasing holes from V-type centers [10,11]. These centers are single or associated with impurities cation vacancies which trapped one or several holes [24]. In magnesium oxide such centers can be formed when the oxide is exposed to high-energy particles, which was not observed in our experiments as the energy of the electron beam (130 keV) was much lower than the threshold value necessary to create cation and anion vacancies in MgO according to the knock-out mechanism (330 keV) [25]. There are also literature data on high concentration of similar centers in non-irradiated MgO samples with high proportion of impurities, which is conditioned by a charge-compensation principle [26]. As the samples we examined contained large amount of three-valent iron impurities, one can hypothesize that a chance of formation in them of cation vacancies which form V-type centers is high. When the samples are irradiated, the charge states of these defects change. As a result of further thermal stimulation and destruction of V-type centers, freeing of holes, whose recombination on the luminescence centers causes TL at 380 K, is observed.

Our results of the measurements of the TL spectrum recorded at T=365 K (Figure 5) support the hypothesis that the TL peak at 380 K has the hole nature. It is seen that a band at 3.1 eV (400 nm) caused by relaxation of F^+-centers dominates in the spectrum [27]. Luminescence of F^+-centers in the TL peak at 380 K in the samples under study can be caused by trapping of the holes released from the traps by F-centers which are transformed into excited F^+-centers with their further radiative relaxation: $F + h^+ = F^+* = F^+ + h\nu$ (3.1 eV). This mechanism has been earlier discussed for TL of anion-defective alumina [2]. In the case of MgO, the presence of the dominating band of F^+-centers may speak for the hole nature of the traps responsible for the TL peak at 380 K, which is in agreement with the data from the literature.

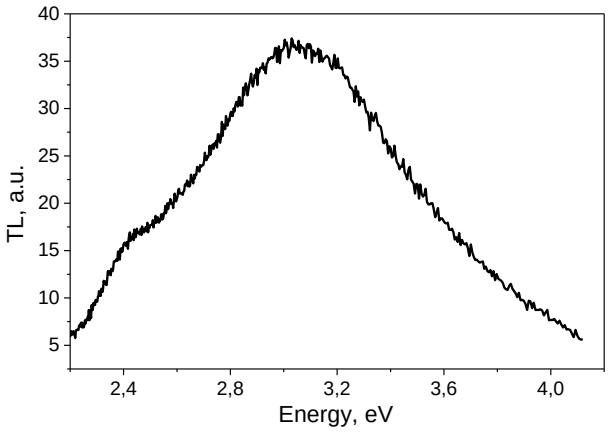

Figure 5. Emission spectrum of the TL peak at 380 K, which was measured at T=365 K

The desensitization effect of TL of this peak under stepped annealing allows hypothesizing on the hole nature of deep traps associated with the TL peaks at 510 and 600 K. Works [10,11] report on the hole nature of the TL peak at 495 K, which is near the peak at 510 K in its temperature position. In these works, the peak at 495 K is associated with V^--centers. There is also an opinion that the TL peak at 615 K is caused by recharging of chromium impurity ions [10].

4. Conclusions

The characteristics of TL associated with deep traps in ultrafine magnesium oxide compacts were studied. It was shown that their thermal treatment in the reducing environment at T=1100–1400 ^oC make the TL yield grow due to formation of F-type centers and cause the grain size increase up to 150 nm. The effects of changes of the TL yield in the peak at 380 K as a result of varying occupancy of deep traps were found. It was shown that TL sensitization of the peak is caused by a competing interaction of the traps of the main TL peak and deep traps capturing the carriers of same sign. A

hypothesis on the predominantly hole nature of the traps responsible for the observed TL peaks of the samples under study was made on the base of the literature data and measurements of the spectral composition of TL.

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